ACID-BASE REACTIONS BETWEEN COMPONENTS IN SODIUM-ALUMINOBOROSILICATE GLASSES

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The effect of coordination groups of boron, aluminum, and silicon on acid-base properties and specifics of the variation in the redox state of copper in boron-containing melts are investigated. An approximate evaluation of acid-base properties of industrial glasses synthesized in an alkaline-aluminoborosilicate system is implemented.

An important role in glass technologies is played by redox processes occurring in melts between variable-valence elements (VVE). Variable-valence elements introduced in clear or tinted glass compositions via materials (iron, sulfur) or via colorant additives (for instance, chromium, copper, etc.) always exist in a glass melt in different valence states interrelated by redox equilibrium (ROE) of the following type [1]:

$$\mathrm{Me}^{n+} + \Delta n/4\mathrm{O}_2 \leftrightarrow \mathrm{Me}^{(n+\Delta n)+} + \Delta n/2\mathrm{O}^{2-},$$

where Δn is the variation in the valence of a cation (1, 2, 3, ..., n).

An uncontrolled shift of the specified equilibrium between different valence forms of VVE has a significant and in some cases a negative effect on the technological (diathermancy and surface tension of a glass melt), optical (coefficient of directed light-transmission), and spectral properties of glasses and modifies their service characteristics and the performance parameters of production lines [2]. Consequently, research on conditions of obtaining and stabilizing a ROE and understanding the factors of variations in the ratio between different valence forms of VVE in industrial melts is of great practical significance.

There exist several practical methods for controlling redox processes in melts (modification of temperature and gas conditions of glass melting and modification of the chemical composition of glass). Ultimately all these methods are intended to impart a certain redox state to the melt, on which implementation of a prescribed ratio of the valence forms of VVE depends [2].

Therefore, to solve technological problems related to optimization of glass-melting and tinting of melts, it is essential to have quantitative methods for estimating the redox state of a glass melt. Such expressions in combination with the traditional representation of compositions as a sum of oxides should in a concise form provide information on specifics of glass structure and properties. Since glass is a complex chemical compound, these expressions can be obtained taking into account the respective shares of components comprising a glass-forming matrix.

Significant differences (more than 100 times in industrial glasses) between the content of main components (glass-forming agents and modifiers) and impurity components (raw material impurities, colorants, clarifiers, gases) make it possible to draw an analogy (in the context of definitions used in inorganic chemistry) between a silicate melt and an ultimately diluted liquid solution [3, 4]. In this case a silicate melt acts as a solvent, and the specified VVE impurities act as a dissolved material. Considering that the acidity (alkalinity) of a solvent, which is quantitatively determined as a pH (pOH) value, has a predominant effect on the valence-coordination state of a dissolved material, the specifics of VVE behavior in melts can be considered in the context of the concept of acid-base relations [4].

The contemporary concept of the nature of acid-base reactions between solution components is based on the assumptions of the Lewis acid-and-base electron theory [3]. According to this theory, any compound (atom, ion, radical, or molecule) capable of supplying a pair of electrons (for instance, an OH^- anion in aqueous solutions) is regarded as a base, and a compound capable of assimilating an electron pair to form a covalent bond is regarded as an acid.

The basicity (acid-base properties) of multicomponent silicate melts can be measured by the activity of free oxygen ions O^{2-} not incorporated in silicon-oxygen groups. Being donors of electrons, these ions differ from other oxygen ion modifications present in melts (bridge oxygen O^0 and nonbridge ion O^-), as the former possess greater mobility and,

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accordingly, are the most active. It is assumed that O^{2-} ions arise in the course of formation and thermal dissociation of alkaline silicates, in accordance with the following scheme [1]:

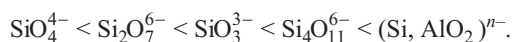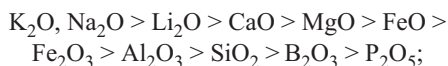$$MeO \cdot mSiO_2 \leftrightarrow MeO + mSiO_2 \leftrightarrow Me^{2+} + O^{2-} + mSiO_2.$$

Among other hypotheses for the character of basicity in silicate glasses, the following concepts are also discussed:

– on simultaneous existence of free oxygen anions in melts with silicon-oxygen ($[SiO_{3/2}]^+$, $[OSiO_{3/2}]^-$) and boron-oxygen ($[BO_{2/2}]^+$, $[OBO_{2/2}]^-$) groups executing acid (positive) and basic (negative) functions [4];

– on total absence of O^{2-} in high-silica melts [1].

The latter assumption motivated a search for correlation dependences between the acid-base properties of melts and the parameters characterizing the chemical reactions of MeO in structural groups (apparent molar refraction of oxygen, ionic degree of the bond, electronegativity, etc.).

A calculation of electronegativity of metal oxides and crystalline silicates performed in [5, 6] made it possible to arrange these compounds in sequences of monotonically increasing acidity (decreasing basicity) [5, 6]:

$$K_2O, Na_2O > Li_2O > CaO > MgO > FeO >$$
$$Fe_2O_3 > Al_2O_3 > SiO_2 > B_2O_3 > P_2O_5;$$

$$SiO_4^{4-} < Si_2O_7^{6-} < SiO_3^{3-} < Si_4O_{11}^{6-} < (Si, AlO_2)^{n-}.$$

It is noted that the higher the value of electronegativity of a compound, the more expressed are its acid properties [5, 6].

A special place in the concept of acid-base relations is given to a correlation between acid-base and redox processes. According to a hypothesis put forward by M. I. Usanovich [3], redox processes show a more complete transfer of electrons from a reducing agent to an oxidizer, whereas in a reaction of an acid with a base, electrons become shared (generalized) between the initial compounds with formation of a covalent bond. This suggests that a redox process is a particular case of an acid-base reaction between silicate melt components.

There is yet no reliable and simple method for determining the acid-base properties of a melt in industrial conditions. Therefore, the existence of a correlation between acid-base and redox processes makes it possible to use impurity oxides as indicators for an indirect estimate of the alkalinity of melts. In this case an increased concentration of VVE of a higher valence will point to increasing alkalinity (decreasing acidity), and vice versa.

The purpose of this study was to select an indicator for quantitative estimation of the acid-base properties of melts and to study the influence of the coordination state of structural groups formed in glasses on the ratio between the valence forms of VVE in a glass melt.

The study was performed on alkaline-aluminoborosilicate glasses. This system is a basis for the majority of optical, chemical laboratory, lighting-engineering, electrova-

TABLE 1

Value Ψ_B	Coordination groups			
	BO_4^{5-}	AlO_4^{5-}	BO_3^{3-}	AlO_4^{9-}
$\Psi_B > 1.00$	Present	Present	Absent	Absent
$1.00 > \Psi_B > 0.33$	The same	The same	Present	The same
$0.33 > \Psi_B > 0.00$	Absent	"	The same	"
$Y_B < 0.00$	The same	Absent	"	Present

cuum, medical, and other types of glass with heightened chemical and thermal resistance. Their structural specifics are determined by the fact that their structure, apart from silicon-oxygen anions (SiO_4^{4-}), contains various flat (BO_3^{3-}) and volume (BO_4^{5-}), (AlO_4^{5-} and AlO_6^{9-}) groups, whose coordination state is related to the structural ratio Ψ_B (Table 1) [1].

$$\Psi_B = (Me_2O - Al_2O_3)/B_2O_3,$$

where Me_2O, Al_2O_3, and B_2O_3 are the molar contents of oxides of alkaline metals, aluminum, and boron, %.

Under positive values of the parameter Ψ_B, the oxygen coordination of boron varies from 3 to 4. Within the range of negative values, the coordination number of aluminum grows from 4 to 6. Structural transformation of aluminum and boron depending on modifications of the glass composition are corroborated by the Raman scattering and x-ray analysis methods [7]. Since most boron-containing glasses of industrial purpose lie within the range of positive values of Ψ_B, the acid-base properties of glasses were investigated at sections A_i and B (where $i = 10$, 15, and 20 mol.% B_2O_3) by varying the content of the main components within the following limits (%): $30.0 - 83.7$ SiO_2, $1.6 - 25.0$ Al_2O_3, $1.6 - 25.0$ Na_2O, $10.0 - 20.0$ B_2O_3.

Table 2 indicates the compositions of the considered glasses (according to synthesis), their molar content of aluminum and boron in different coordination groups, as well as variation intervals for the parameter Ψ_B. The VVE additives (indicators) used to indicate modifications in the acid-base properties of glasses were copper and chlorine introduced into the glass compositions in constant quantities.

In studying changes in the ROE state, it was taken into account that the optical density of glass with copper additives at a wavelength of 790 nm is proportional to the content of bivalent (in the oxidized state) copper Cu^{2+} [8]. Univalent copper in the compound CuCl absorbs at a wavelength of 380 nm, and metallic copper Cu^0 (the reduced state) has an absorption band at 600 nm.

The acid-base properties of glasses were estimated using the following parameters:

– effective electronegativity index [9]:

$$EN_{ef} = \sum EN_i \cdot a_i / \sum a_i,$$

where EN_i is the electronegativity of electropositive elements in glass (determined according to the data in [3]); a_i is the atomic content of the component, %;
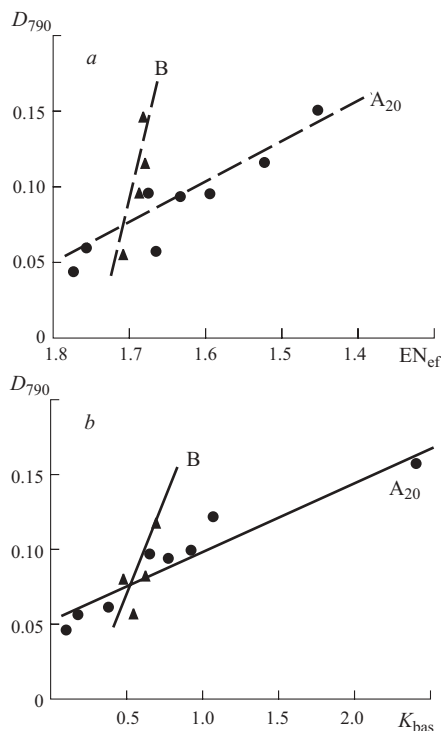
Fig. 1. Optical density variation at the maximum of the absorption band of Cu^{2+} (D_{790}) depending on the basicity coefficient (*a*) and effective electronegativity (*b*).

– glass basicity coefficient [10]:

$$K_{bas} = \frac{4.6X_1 + 4.7(X_2 - X_1)}{0.82X_3 + 1[X_4 - (X_2 - X_1)]}, \qquad (1)$$

where X_1, X_2, X_3, and X_4 is the molar content of aluminum, sodium, silicon and boron oxides, respectively, %.

Figure 1 indicates the dependences of absorption intensity (in optical density units) for a wavelength of 790 nm on effective electronegativity and the glass basicity coefficient in glasses of series A_{20} and B. It can be seen that the experimental points are arranged near the straight lines, which points to an increasing content of oxidized copper Cu^{2+}, while K_{bas} increases and EN_{ef} decreases. Thus, the basicity of
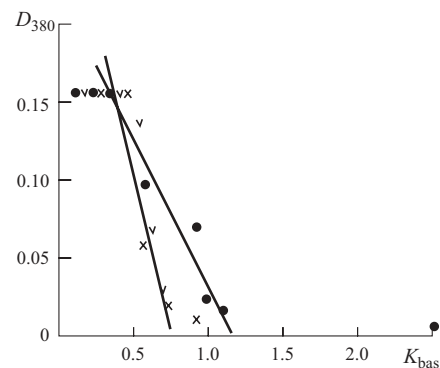

Fig. 2. Optical density variation at the absorption band maximum of CuCl (D_{380}) depending on the basicity coefficient: •) A_{20}, 20% B_2O_3; ×) A_{15}, 15% B_2O_3; v) A_{10}, 10% B_2O_3.

glasses is directly proportionate to K_{bas} and inversely proportionate to EN_{ef}.

A comparison of dependences $D_{790} = f(EN_{ef})$ and $D_{790} = f(K_{bas})$ indicates the symbatic character of their variation, which indicates a sufficient level of reliability in estimating the acid-base properties of the glasses using these coefficients.

In series A_{20}, the decrease in basicity (an increase in K_{bas}) is related a decreased concentration of silicon-oxygen anions SiO_4^{4-} and an increased content of AlO_4^{5-} groups (Table 2), which leads to a transition from univalent copper Cu^+ in glass to bivalent copper. A similar dependence was observed in glasses of series A_{15} and A_{10} (Table 2 and Fig. 2). At the same time, the angle made by the straight lines related to A_{10} and A_{15} glasses is sharper than the angle made by the line related to the glass of A_{20} series, which shows that in a more acid medium (A_{20}, 20% BO_3^{3-}) an increase in basicity has a slower effect on oxidation of copper than in glasses of the A_{15} and A_{10} series.

The increase in basicity in glasses of series B is due to a respective decrease in the concentration of groups BO_4^{5-} (Fig. 1 and Table 2) at the expense of a respective decrease in the concentration of coordination groups BO_3^{3-} and AlO_4^{5-}. The straight lines indicated (Figs. 1 and 2) show the difference in the acid-base properties of the groups incorporated

TABLE 2

Glass series	Variation of molar content of components (structural groups),* %							Variation interval of parameters		
	SiO_2	Na_2O	Al_2O_3		B_2O_3			Ψ_B	EN_{ef}	K_{bas}
			total	including AlO_4^{5-}	total	including				
						BO_4^{5-}	BO_3^{3-}			
A_{20}	74.00 – 30.00	3.00 – 25.00	3.00 – 25.00	3.00 – 25.00	20.00	–	20.00	0.0	1.79 – 1.43	0.19 – 2.51
A_{15}	78.16 – 62.96	3.40 – 11.00	3.40 – 11.00	3.40 – 11.00	15.04	–	15.04	0.0	1.80 – 1.65	0.20 – 0.70
A_{10}	83.73 – 63.53	4.10 – 13.20	4.10 – 13.20	4.10 – 13.20	10.07	–	10.07	0.0	1.79 – 1.63	0.24 – 0.96
B	68.80	5.60 – 9.60	5.60 – 9.60	5.60 – 9.60	20.00	0.00 – 7.00	20.00 – 13.00	0.0 – 0.4	1.73 – 1.67	0.33 – 0.66

* The content of boron and aluminum incorporated in structural groups BO_3^{3-}, BO_4^{5-}, and Al_4^{5-} was calculated in accordance with the data in [1].

TABLE 3

Parameter	Structural group				
	BO_3^{3-}	SiO_4^{4-}	BO_4^{9-}	AlO_4^{5-}	NaO_6^{6-}
Strength of Me – O single bond, kJ/mole [11]	523	426	393	387	84
Cation field force [12]	1.63	1.57	1.34	0.96	0.19

in the glass structure. The acidity of glass melts in the $Na_2O - Al_2O_3 - B_2O_3 - SiO_2$ system is most effectively decreased by an increased concentration of boron and aluminum in four coordination, and to a much smaller extent by an increased content of SiO_4^{4-} groups. In contrast to the above examples, the acidity of glass grows with an increasing concentration of BO_3^{3-} groups.

The obtained data make it possible to rank the coordination groups present in sodium-aluminoborosilicate glasses in order of descending acidity (increasing basicity):

$$BO_3^{3-} > SiO_4^{4-} > BO_4^{5-} > AlO_4^{5-} > NaO_6^{6-}. \qquad (2)$$

Note that sequence (2) coincides with ranking of structural groups according to their parameters characterizing the chemical bond specifics, for example, the strength of Me – O single bond, the force of cation field, etc. (Table 3).

The main difference between the proposed parameters for estimating basicity consists in the fact that EN_{ef} gives a simplified notion of the effect of composition on the modification of acid-base properties of glass, whereas K_{bas} takes into account the specifics of coordination transformations of boron and aluminum. The numerator of the equation for calculation of K_{bas} adds up the contents of the structural groups of aluminum X_1 and boron $(X_2 - X_1)$ existing in four coordination and having alkaline properties in the $Na_2O - Al_2O_3 - B_2O_3 - SiO_2$ system (Fig. 1, straight lines A_{20} and B). The denominator of equation (1) includes the contents of the groups with a more acid character than in the first case. Here X_3 correlates with the silicon oxide content in four coordination and the difference $[X_4 - (X_2 - X_1)]$ correlates with the boron content in the form of BO_3^{3-}. The summands in ex-
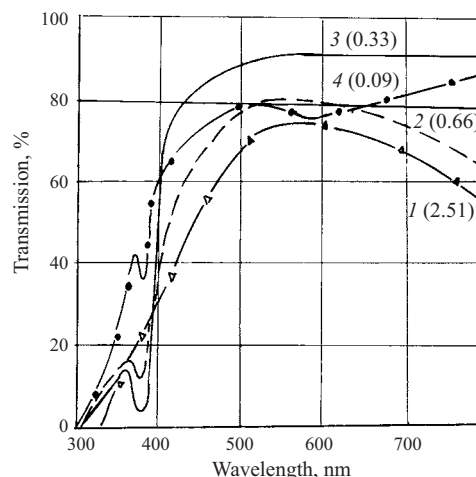

Fig. 3. Spectral transmission curves of glasses. Curve numbers correlate with glass compositions, and their basicity coefficients are indicated in brackets.

pression (1) are preceded by relative coefficients of the activity of oxygen anions present in the structural groups of aluminum, boron, and silicon. A method for their calculation is described in [10].

Table 4 represents the optical characteristics of glasses $1 - 4$ with different levels of acid-base properties, and Fig. 3 represents the spectral curves of light transmission variation in these glasses. A high-alkali glass of composition 1 ($K_{bas}=$ 2.51) is tinted green. Copper in this composition is present in the highest valence form (Cu^{2+}), which is corroborated by an absorption band at a wavelength of 790 nm. A similar tint is seen in glass 2 ($K_{bas} = 0.66$). In contrast to glass 1, a more acid glass 2 has an insignificant quantity of univalent copper bonded with chlorine in the CuCl compound (a band at a wavelength of 380 nm). The same compound is contained in glasses 3 ($K_{bas} = 0.33$) and 4 ($K_{bas} = 0.09$). It is typical that the specified compositions virtually do not contain oxidized copper (low value of D_{790}). At the same time, an ultra-acid glass of composition 4 has a reddish tint and absorption bands at wavelengths of 380 and 600 nm indicating the simultaneous presence of weakly reduced (Cu^+) and strongly reduced (Cu^0) forms of copper.

TABLE 4

Glass composition	Molar content,* %			Basicity coefficient	Optical density for wavelength, nm		TCLE, 10^{-7} K^{-1}	Tint
	SiO_2	Al_2O_3	Na_2O		780	380		
1	30.0	25.0	25.0	2.51	0.15	0.07	92.0**	Green
2	68.8	1.6	9.6	0.66	0.12	1.20	66.0	The same
3	68.8	5.6	5.6	0.33	0.06	1.60	52.3	Clear
4	76.8	1.6	1.6	0.09	0.05	1.07	40.6	Red

* B_2O_3 content in all composition was 20.0%.

** According to a calculation presented in [8].

TABLE 5

Glass composition* [7]	Molar content, %						Effective electronegativity	Basicity coefficient	TCLE, 10^{-7} K^{-1}	Heat resistance, °C	Dielectric loss $\tan \theta \times 10^4$	Relative dielectric permittivity
	SiO$_2$	B$_2$O$_3$	Al$_2$O$_3$	Na$_2$O	K$_2$O	BaO						
No. 17	83.54	11.87	–	2.44	0.80	1.35 PbO	1.82	0.28	39.5	230	22	4.20 – 4.70
3S-9	70.11	23.14	0.93	5.50	0.32	–	1.75	0.36	35.5	200	28	4.20 – 4.60
3S-8	70.67	21.05	1.88	3.82	2.58	–	1.72	0.40	48.0	220	32	–
3S-5	71.39	18.66	2.21	4.05	3.69	–	1.74	0.53	49.0	180	40	5.35
S88-13**	76.31	1.43	–	8.84	3.46	0.70	1.56	2.40	89.0	130	45	–

* To simplify the calculation of the basicity coefficient, alkaline and alkaline-earth metal oxides are accounted as Na$_2$O.

** Glass C88-13 contained as well 4.91%CaO and 4.35% MgO.

Along with variations in the spectral properties of glasses *1 – 4*, a significant variation is registered in their physical characteristics depending on the basicity coefficient. For examples, as the K_{bas} varies from 0.09 to 2.51, the TCLE of glass increases from 40 to 92×10^{-7} K^{-1}.

As most industrial boron-containing glasses are within the range of positive values of Ψ_B, the indicators of acid-base properties of melts can be used for preliminary estimate of the effect of glass compositions on the direction of redox equilibrium in VVE and certain service (for instance, thermal, electrical, etc.) parameters of glass.

Table 5 shows the compositions of some industrial-purpose electrovacuum glasses taken by way of example from [8]. They are ranked in order of descending acidity (increasing basicity). The variation of K_{bas} in these compositions is within the limits of 0.28 – 2.40. In contrast to the high-alkali glass S86-13 ($K_{bas} = 2.40$), glasses with increased acidity (No. 17, 3S-9, 3S-8, and 3S-5) have higher melting and clarification temperatures, low TCLE values $(35 – 49) \times 10^{-7}$ K^{-1}, high thermal resistance (200 – 250°C), and low dielectric loss and relative dielectric premittivity.

The criteria developed on the basis of the concept of acid-base relations have been successfully used in developing copper-haloid photochromy glass compositions and in studying the diathermancy variation dynamics in melts upon introducing a catalyst and optimization of glass-melting in continuous sheet glass production. The use of these criteria makes it possible to objectively estimate the nature of modification of acid-base properties of melts in various technological processes.

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